IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Karin Schlicht et al.
Serial No. :	10/665,412
For:	METHOD FOR THE REMOVAL OF AN IMAGING LAYER FROM A SEMICONDUCTOR SUBSTRATE STACK
Filed:	September 18, 2003
Examiner:	Kripa Sagar
Art Unit:	1756
Confirmation No. :	4389
Customer No. :	27,623

Attorney Docket No.: 335.7697USU

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. §1.131(b)

Dear Sir:

Karin Schlicht, and Mario Reybrouck applicants in the above-identified patent application, declare as follows:

1. That sometime prior to April 6, 2002, we conceived a rework process for removing an imaging layer from a substrate stack comprising a substrate, an underlayer adjacent to the substrate, and an imaging layer comprising silicon placed adjacent to the underlayer.

The above process involves the steps of: (a) contacting the substrate stack with an imaging layer removal solvent; (b) removing the imaging layer with an imaging layer removal solvent thereby forming a substrate/underlayer stack, wherein said imaging layer removal solvent is selected from glycol ethers, ketones, esters, lactates, dimethylsulfoxide

(DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methyl tetrahydrofuran, dioxane, tetrahydropyran, ethyl tetrahydropyran-4-acetate, methyl tetrahyd ropyran-4-methanol, tetrahydropyran-4-one, n-butyl acetate, n-amyl acetate, and any combinations thereof; and (c) removing the imaging layer removal solvent from the substrate/underlayer stack after the imaging layer is removed.

2. We also conceived a lithographic imaging rework process for correcting one or more defects on an imaging layer on a substrate stack. The substrate stack comprises a substrate, an underlayer adjacent to a substrate, and an imaging layer comprising of silicon adjacent to the underlayer.

The above process comprises the steps of: (a) contacting the substrate stack with an imaging layer removal solvent selected from glycol ethers, ketones, esters, lactates, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methyl tetrahydrofuran, dioxane, tetrahydropyran, ethyl tetrahydropyran-4-acetate, methyl tetrahydropyran-4-methanol, tetrahydropyran-4-one, n-butyl acetate, n-amyl acetate, and any combinations thereof; (b) removing the imaging layer with the imaging layer removal solvent, thereby forming a substrate/underlayer stack; (c) removing the imaging layer removal solvent from the substrate/underlayer stack after said imaging layer is removed; (d) coating the substrate/underlayer stack with a new imaging layer; (e) exposing the new imaging layer to radiation; and (f) developing the new imaging layer.

3. In addition, we concieved a rework process for removing an imaging layer from a substrate stack, said stack comprising a substrate, an underlayer adjacent to said substrate, and an imaging layer comprising silicon adjacent to said underlayer.

The process comprises the steps of (a) contacting the substrate stack with an imaging layer removal solvent; (b) removing said imaging layer with the imaging layer removal solvent thereby forming a substrate/underlayer stack, wherein the imaging layer removal solvent is selected from the group of glycol ethers, ketones, esters, lactates, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), methyl tetrahydrofuran, dioxane, tetrahydropyran, ethyl tetrahydropyran-4-acetate, methyl tetrahydropyran-4-methanol, tetrahydropyran-4-one, n-butyl acetate, n-amyl acetate, and

any combinations thereof; (c) rinsing said imaging layer removal solvent from the substrate/underlayer stack with a rinse solution after the imaging layer is removed; and (d) baking the substrate/underlayer stack to remove said rinse solution.

4. Attached hereto is Exhibit A which is a Company Internal Report written by Karin Schlicht sometime prior to April 6, 2002 setting forth evidence of the above rework process using propylene glycol monomethyl ether acetate (PGMEA) as a solvent, for example, indicated by "RER 600." The report demostrates inventor's possesion of the inventive concept of using the PGMEA solvent system in combination with a substrate for stipping the imaging layer without a bake step as declared under section (1) above.

5. Attached hereto is Exhibit B which is a Company Internal Report written by Karin Schlicht sometime prior to April 6, 2002 setting forth evidence of the above rework process using a propylene glycol monomethyl ether acetate (PGMEA)/EL mixture, and PGME as solvents. The report demostrates the inventor's possesion of the inventive concept of using a PGMEA solvent system in combination with a substrate for stipping the imaging layer with a bake step as declared under section (2) above.

6. Attached hereto is Exhibit C which is a Company Document created and presented by Karin Schlicht prior to April 6, 2002 setting forth evidence of the above rework process, as a whole, using propylene glycol monomethyl ether acetate PGMEA/EL mixtures and PGMEA/PGME/MPK compositions as a solvents. The report demostrates the inventor's possesion of the inventive concept of using a PGMEA solvent system in combination with a substrate for stipping the imaging layer with relevant bake steps as declared under section (1-3) above.

7. We further declare that all statements made herein of our knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Declared at E. Providence RI, U.S.A. this 13th day of December, 2004.

Karin Schlicht, Karin Schlicht

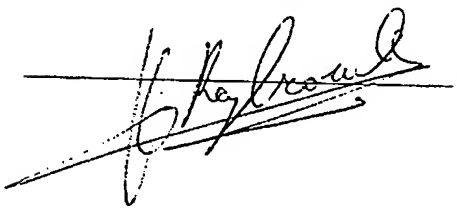
Declared at _____, Belgium this ____ day of _____, 2004.

_____ Mario Reybrouck.

Declared at _____, U.S.A. this ____ day of _____, 2004.

_____ Karen Schlicht,

Declared at Zele, Belgium this 10 day of December, 2004.



_____ Mario Reybrouck.

EXHIBIT A

Formulated Products

ARCH Chemicals, Inc.

East Providence, RI

Report Title:	248 TIS Imaging Layer Rework
Requested By:	Internal

Subject:	Screening materials to rework 248 TIS Imaging Layer
Conclusions:	A rework process with RER 600 worked on the FTCU, but needs further optimization for the new underlayer. RER 651 and a PGMEA/EL mixture resulted in clean imaging after 1x rework.
Keywords:	TIS 248, TIS 193, Rework, RER 600, RER 651, Imaging Layer

Report Written by: Karin Schlicht

Work Performed by: Jeff Eisele, Pat Morra, Ken Uhnak, Karin Schlicht

Classification: Restricted to ARCH.

Introduction:

Work has been done my Mario Reybrouck at IMEC on the 248 nm TIS system. The following results were obtained:

RER600 was successfully used on the FFA UL. This was a 5 – 60 min. immersion process, followed by a water rinse, and a 90" proximity bake @ 100 C. The 100 C temperature was chosen to drive off excess water. After re-imaging a new IL the process window was virtually identical. FTIR results also showed that the UL was unchanged after the rework process.

Objective:

Re-create IMEC results at QP and find new solvent system that can be marketed for TIS rework.

Experimental:

The following factors will be studied:

1. "old" FFA vs new imaging system
2. Bake step after stripping of the UL
3. Water rinse (Cascade rinse followed by spin rinse dryer)

The following experimental matrix will investigate these variables as well as look into new solvents mixtures:

Imaging System	Bake Temp	Stripper
Old IL/UL	100 C	RER600
new IL/UL	100 C	RER600
new IL/UL	205 C	RER600
new IL/UL	100 C	RER651
new IL/UL	100 C	PGMEA/EL
new IL/UL	100 C	PGMEA/MPK
new IL/UL	on track/no water rinse	RER600

Two wafers were processed for each condition. Most wafers were stripped in a bath with agitation at room temperature. A DNS coating track was used to strip wafers for the track process. Here RER 600 was applied dynamically to strip off the imaging layer. These wafers were subsequently spun dry, but no additional bake step was used.

Best energy and focus were found for the control wafers (no rework). SEM pictures for the reworked wafers were then taken at the same energy and focus settings.

Results:

SEM micrographs are attached to the PDF version of this report. Results from the duplicate wafers show that there is noise in the stripping process.

RER 600 was used to investigate the influence of the dehydration bake and a track process without water rinse or dehydration bake.

The track process resulted in clean profiles without footing on one of the wafers, but had scumming on another. This shows that the process works but needs optimization. (RER 600 was hand dispensed). Wafers with a 205 C dehydration bake had no scumming between the lines, but some footing is visible. At the 100 C bake images showed bad footing.

Work done on the FTCU ("old") with RER 600 showed comparable results to the control.

RER 651 and a mixture of PGMEA and EL resulted in clean imaging after rework, while a mixture of PGMEA and MPK showed severe scumming. I did not expect this degee of scumming since RER 651 also contains MPK.

Conclusions:

A rework process with RER 600 worked on the FTCU, but needs further optimization for the new underlayer. RER 651 and a PGMEA/EL mixture resulted in clean imaging after 1x rework.

Future Work:

1. This work needs to be repeated for the 193 IL/UL.
2. Repeated rework with best stripper solution.
3. Test UL integrity by FTIR.

EXHIBIT B

Formulated Products

ARCH Chemicals, Inc. East Providence, RI

Report Title: 193 IL Removal – Part 1

Requested By: Internal

Subject: Test IL removal chemistries with TIS 193 nm system. Chemistries chosen were successful with the TIS 248 nm system.

Conclusions: PGMEA as the solvent to remove the imaging layer appears to cause adhesion failure after subsequent processing. However, when PGMEA is mixed with EL or PGME scumming can occur. Optimization may be possible.

Keywords: TIS 193, IL rework, TIS2200UL, TIS2000IL-05

Report Written by: Karin Schlicht

Work Performed by: Karin Schlicht, Pat Morra, Paul Berard

Classification: Restricted to ARCH.

Distribution: ARCH employees

Introduction:

The imaging layer rework with the TIS 248 nm system was successful with RER651 and a PGMEA/EL mixture[1]. RER 600 also showed promise. In this experiment we are examining if the same chemistries can be used for the rework of the imaging layer of the TIS 193 nm system.

Description of Procedure:

The following experimental matrix was employed:

Chemical	Strip Time [minutes]	Dehydration Bake Temperature [°C]
PGMEA	5	105
PGMEA	5	205
PGMEA	0.5	None*
PGMEA/MPK 99/1	5	105
PGMEA/EL 90/10	5	105
RER 651	5	105
RER 651	10	105
RER 651	20	105

* Track process

Wafers were processed as follows:

1. Wafers processed through development according to the lithographic process listed below in an amine controlled clean room environment.
2. All, but one of the wafers had the IL stripped according to the experimental plan in a non-amine controlled clean room chase area. Stripping was done in a batch mode by immersion. This was followed by a cascade water rings and spin rinse drying. One wafer was stripped on the SVG coat module applying the strip solution on a wafer while spinning @ 500 rpm.
3. Re-imaging according to the lithographic process. Control wafers were imaged only once.
4. SEM micrographs were taken at best energy and focus found for the control wafers (profile and CD measurements only)

Materials and Lithographic Process Parameters:

Parameter	Value
TIS 2200UL lot	K007583
TIS 2200UL process	**Parameter** **Value** Coating Equipment Optitrak Film Thickness 5000 Å Film Cure 70" @ 205 °C
TIS2000IL-5 Lot	K007544
TIS2000IL-5 process	**Parameter** **Value** Coating Tool SVG Film Thickness 2350 Å Soft bake 60" @ 135 °C Exposue tool 193 Microstep Exposure Energy 18 mJ/cm^2 Develop Tool SVG PEB 60" @ 125 °C Developer OPD 262

	Develop process 7"/58" stream/puddle SEM Tool Hitachi 4100 or 4200

Results:

The immersion process with PGMEA resulted in adhesion loss with both the 105 °C and 205 °C dehydration bakes. The formulation with 1 % MPK added the PGMEA had resulted in the same failure. All other conditions, including the PGMEA strip on the SVG track, resulted in severe scumming. (See attached SEM micrographs)

At this point it is not clear if the solvent treatment or any of the other processing steps is the cause for the lifting or the scumming. The processing will be studied in a separate experiment.

Conclusions:

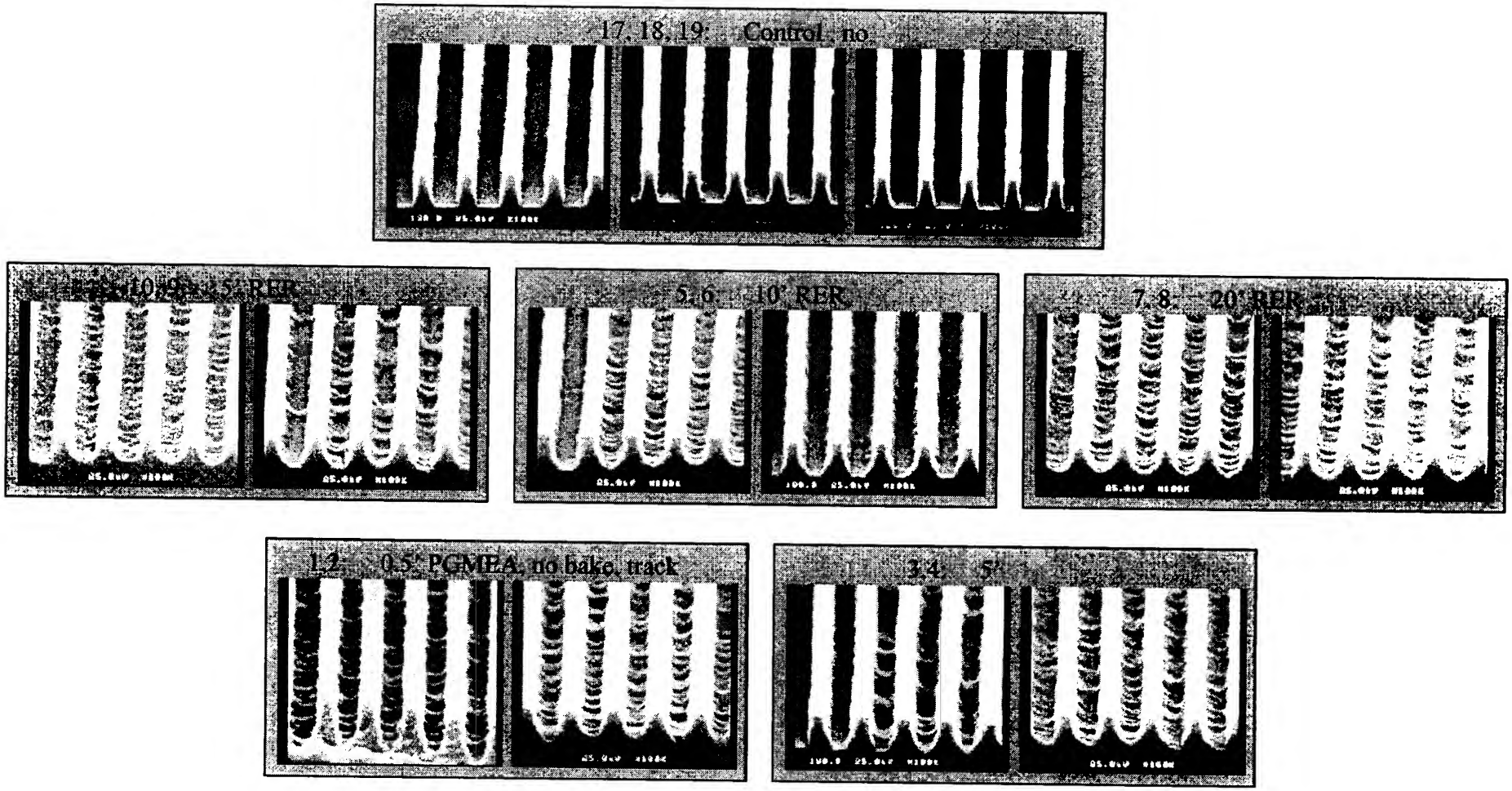
PGMEA as the solvent to remove the imaging layer appears to cause adhesion failure after subsequent processing. However, when PGMEA is mixed with EL or PGME scumming can occur. Optimization may be possible.

Reference:

(1) Internal report issued by Author "248 TIS Imaging Layer Rework", Nov. 29th 2001
(2) Work Request 1212-3290

TIS2000IL-5 Rework (193nm)

130 nm images after 1 x rework



WR12123290

EXHIBIT C

TIS 2000 Rework/Cleaning

Karin Schlicht

248/193 TIS Cleaning Projects

248 SYSTEM

- Imaging Layer removal
- UL removal
- Clean after UL etch
- Clean after pattern transfer

193 SYSTEM

- Imaging Layer removal
- UL removal
- Clean after UL etch
- Clean after pattern transfer

248 IL LSM-96-006 Removal

Work done at QP and IMEC

LSM-96-006 Rework (248nm)

Materials and Lithographic Process Parameters (QP)

UL Process

Material	lot K007553
Cure process	70" @ 205 °C
Film Thickness	5000 Å

IL Process

Material	lot K007528
Soft Bake	90" @ 135 °C
Film Thickness	2350 Å
Exposure tool	Canon EX6
	NA/σ 0.65/0.8/0.5
Exposure E/F	to match control
PEP	90" @ 125 °C
Developer	OPD 262
Develop process stream/puddle	7"/58"
SEM analysis	by cross-section
	Hitachi 4100/4200

LSM-96-006 Rework (248nm)

Base Rework Process Flow (QP)

- Coat UL
- Image 1st layer
  - Coat IL
  - Expose IL
  - Develop IL
- Strip IL
  - Immerse in solvent
  - Cascade water rinse
  - Spin Rinse dryer
  - Dehydration Bake (DHB)
- Image 2nd layer
  - Coat IL
  - Expose IL
  - Develop IL
- SEM Analysis
  - Get best Energy and Focus from controls
  - Take SEM from samples @ best E/F from control wafers

LSM-96-006 Rework (248nm)
UL Film Thickness Retention after Stripping

248nm **TIS248UL-01-50, lot= K007590**
TSI248IL-01-23, lot= K007570-F04

Fth-measurements **after 5min RER 600**

Wafer	before	Filmthickness	st-dev	3 sigma	min	max	range
DO6	550.84nm	550.45	1.454	4.362	547.84	554.63	6.79

after 5min RER 651

Wafer	before	Filmthickness	st-dev	3 sigma	min	max	range
D08	551.44nm	551.77	1.648	4.944	549.03	554.23	5.2

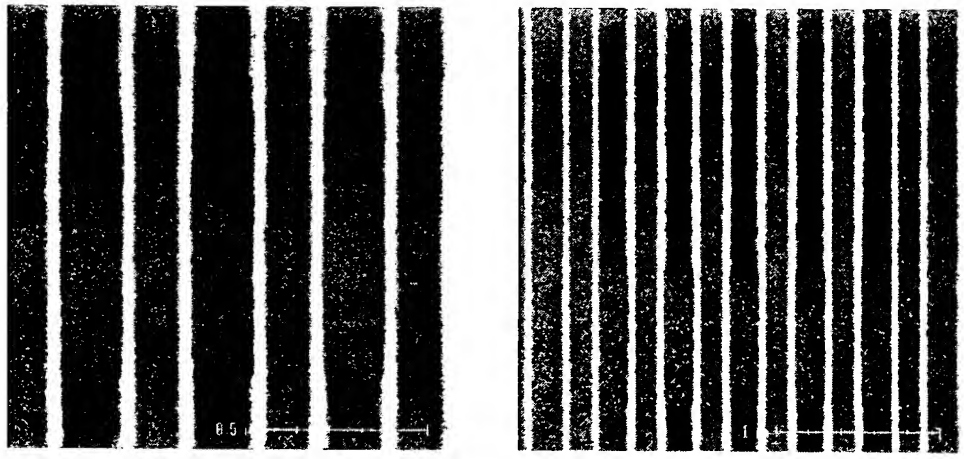
* Wafers after a few seconds clean (visual inspection)

By Mario Reybrouc/IMEC

248nm TIS Rework

T010844 D14 RER600

T010844 D15 RER651

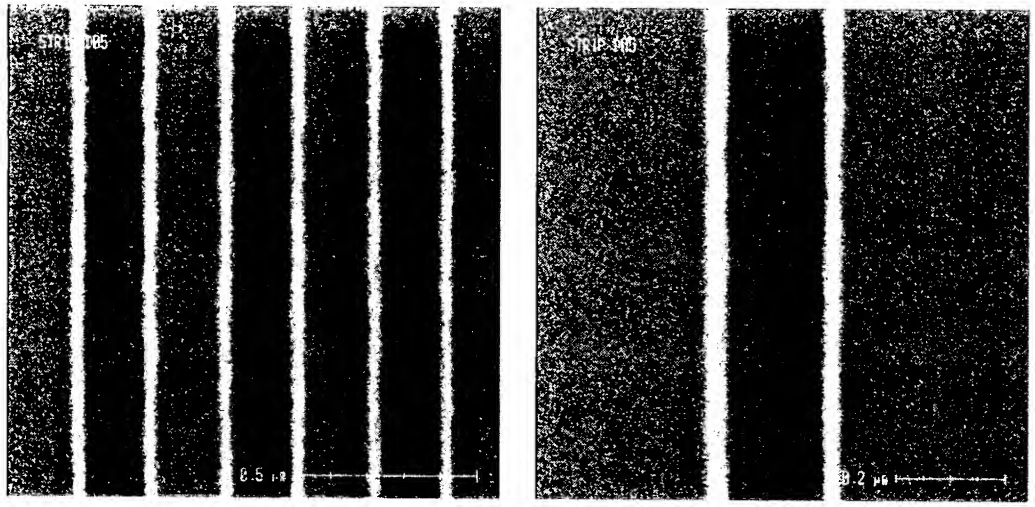


Strip248nm
300nm IL K007570-F04 -550nm K007590
TM99DF_TDF_V01
Trench 200nm
E=30 mj/cm2/2
F=0.1/0.1
NA 0.63 Sigma 0.5

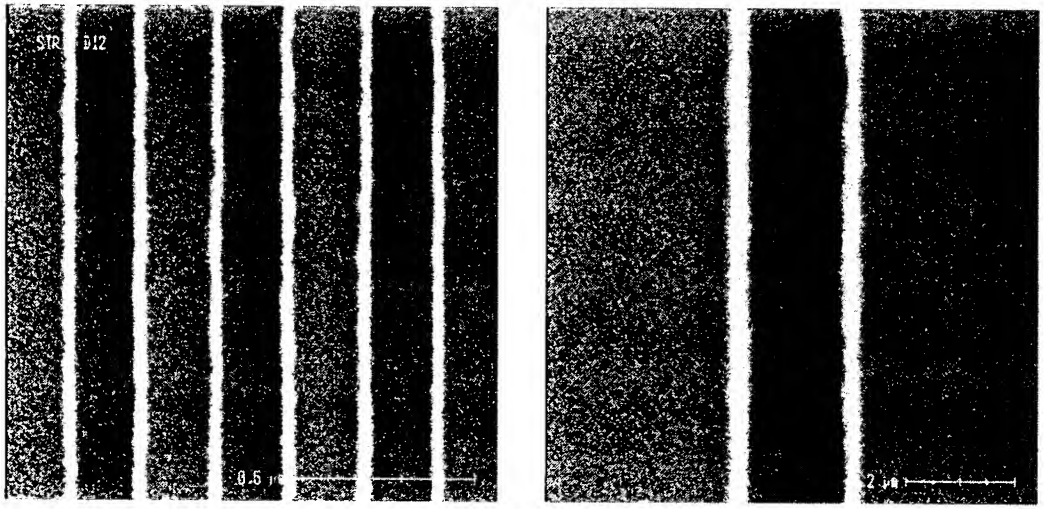
After 2X rework

248nm TIS Rework

T010844 D15 RER651



T010844 D14 RER600



Strip 248nm
300nm IL K007570-F04 - 550nm K007590
TM99DF_TDF_V01
Trench 200nm
E=30 mJ/cm²/2
F=0.1/0.1μm
NA 0.63 Sigma 0.5

After 3X rework

LSM-96-006 Rework (248nm)

200 nm images after 1 x rework

Process Window for RER600 and RER651

RER 600

Rework	Expose Latitude [%]			DOF [um]		
	Dense	Iso	Focus [um]	Dense	Iso	Energy [mJ/cm2]
none	20.2	24.6	0.1	0.7	0.6	36
1 X	19.9	25.2	0.1	0.55	0.6	34
2 X	17.6	23.3	0.1	0.55	0.5	34
3 X	18.1	25.3	0.1	0.55	0.5	34

RER 651

Rework	Expose Latitude [%]			DOF [um]		
	Dense	Iso	Focus [um]	Dense	Iso	Energy [mJ/cm2]
none	20.2	24.6	0.1	0.7	0.6	36
1 X	23.7	25.2	0.1	0.7-0.8	0.6	36-38
2 X	18.7	23.1	0.1	0.4	0.5	34
3 X	22.3	32.2	0.1	0.7	0.5	36

Data generated by Mario Reybrouck at IMEC

193 IL TIS2000 IL-5 Removal

Work done at QP and IMEC

TIS2000IL-5 Rework (193nm)

Materials and Lithographic Process Parameters (QP)

UL Process

Material	lot K007583
Cure process	70" @ 205 °C
Film Thickness	5000 Å

IL Process

Material	lot K007544
Soft Bake	60" @ 135 °C
Film Thickness	2350 Å
Exposure tool	193 ISI Microstep
Exposure E/F	to match control
PEP	60" @ 125 °C
Developer	OPD 262
Develop process	7"/58" stream/puddle
SEM analysis	by cross-section Hitachi 4100/4200

TIS2000IL-5 Rework (193nm)

Base Rework Process Flow (QP)

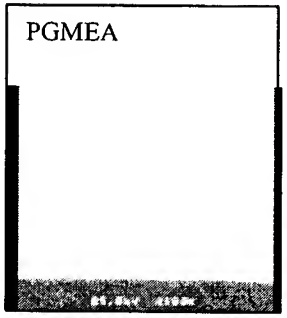
- Coat UL
- Image 1st layer
  - Coat IL
  - Expose IL
  - Develop IL
- Strip IL
  - Immerse in solvent
  - Cascade water rinse
  - Spin Rinse dryer
  - Dehydration Bake (DHB)
- Image 2nd layer
  - Coat IL
  - Expose IL
  - Develop IL
- SEM Analysis
  - Get best Energy and Focus from controls
  - Take SEM from samples @ best E/F from control wafers

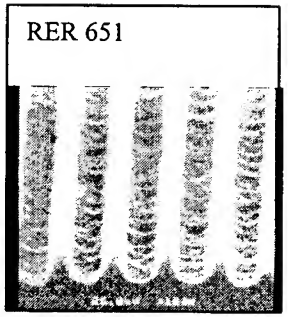
TIS2000IL-5 Rework (193nm)

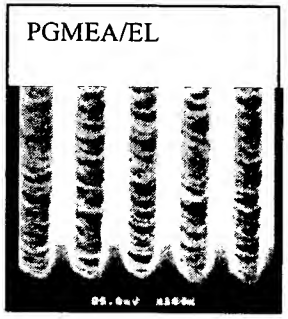
130 nm images after 1 x rework

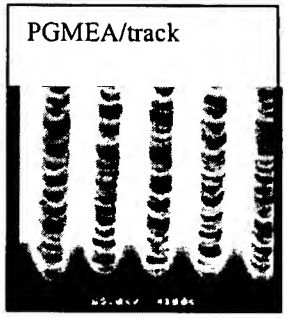
Summary

•Full 1st Layer Image Step
•5' strip, except for track process
•105 °C DHB

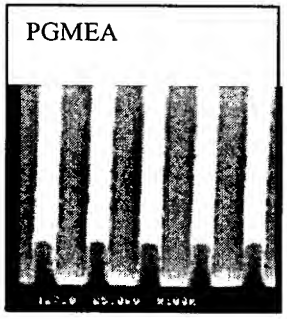


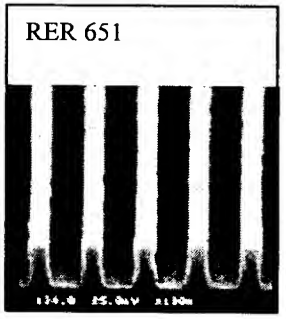


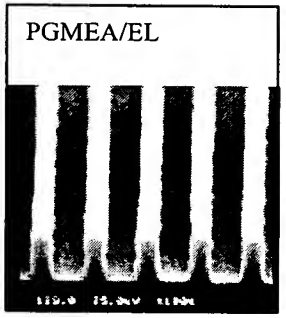


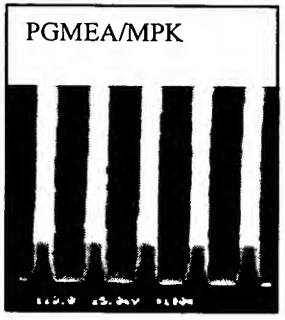


•1st Layer: **coat only**
•2' strip
•150 ° DHB

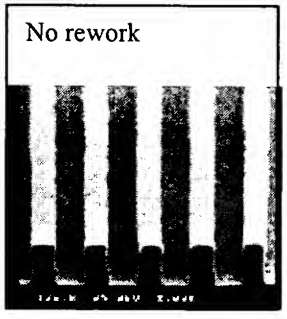


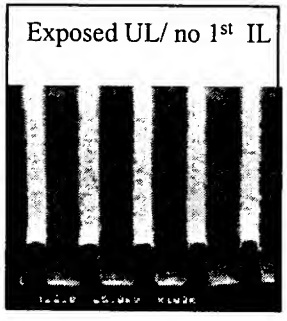


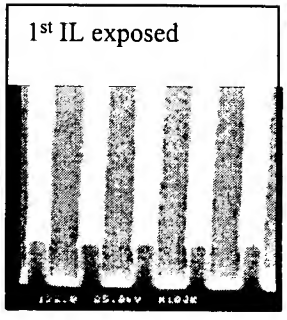


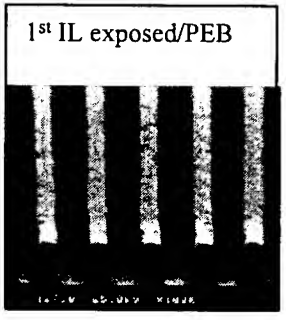


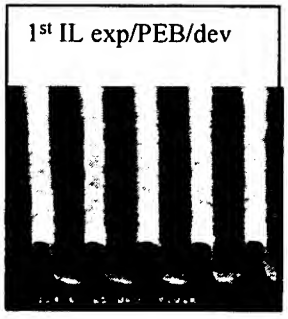
•5' strip w/PGMEA
•150 ° DHB











TIS2000IL-5 Rework (193nm)

Processing Conditions Studied with Good Results

Summary

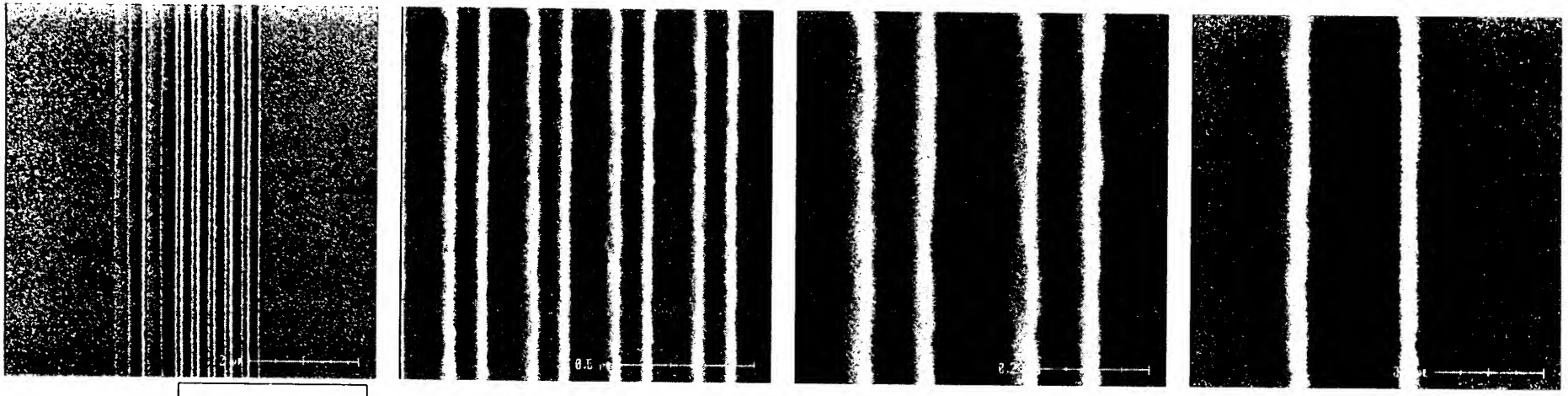
Process Conditon	Ranges	Comments
DHB	105-205 C	UL only; @ 205 C about 30 A Film Thickness Loss
UL left in chase near strip station	up to 48 hours	UL only
DI water rinse	Cascade/spin rinse dry	UL only
Developer	with and w/o PEB	UL only
HF dip	up to 5 minutes	UL only
UL cure time	60-120 seconds	1st IL coat only
DHB	105 - 180 C	1st IL coat only
Strip time	1-5 min	IL coat only/PGMEA strip
Imaging steps	exposure through PEB	UL only or UL/IL stack

Strip 193nm
265nm IL K007547 - 550nm K007563T
TM99DF_TDF_V01
Trench 150nm
E=9 mJ/cm2/0.1
F=0.1/0.1
NA 0.63 Sigma 0.5 **after 1X rework**

193nm TIS Rework

193nm TIS (2*bake steps before exposure)

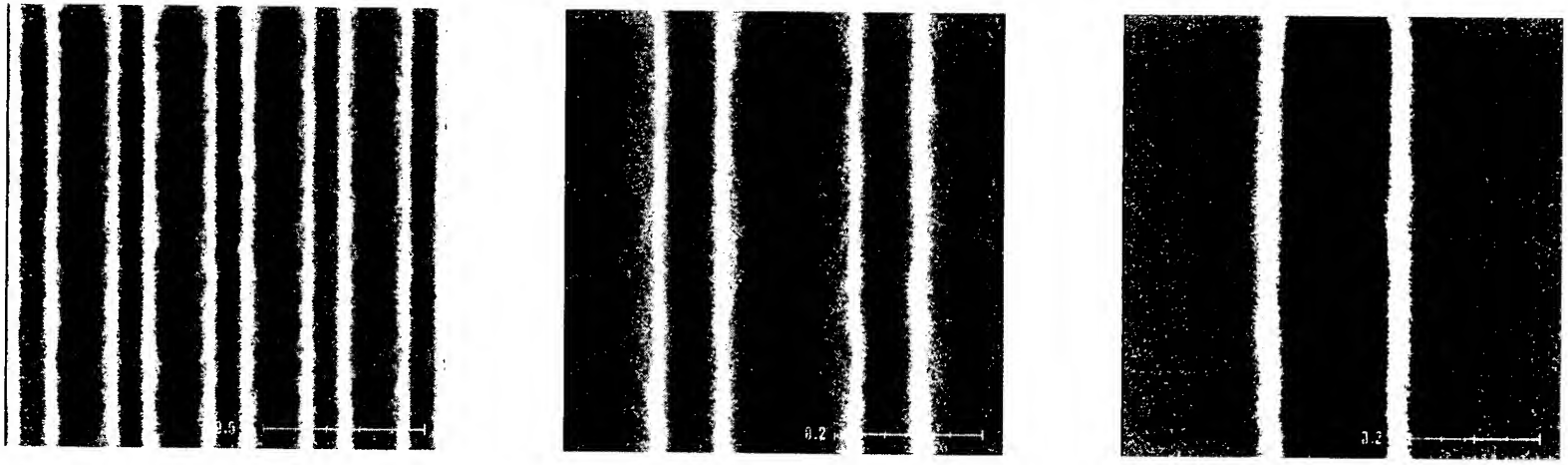
T010385 D17 RER600



E=9.4 mj/cm2

T001153 D10 RER651

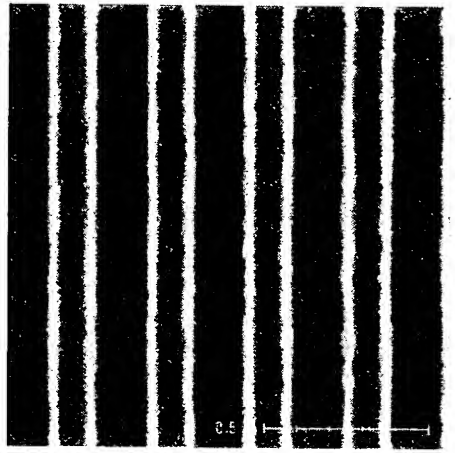
Two bake steps before exposure after rework:
* 105°C/90"
* 205°C/90"

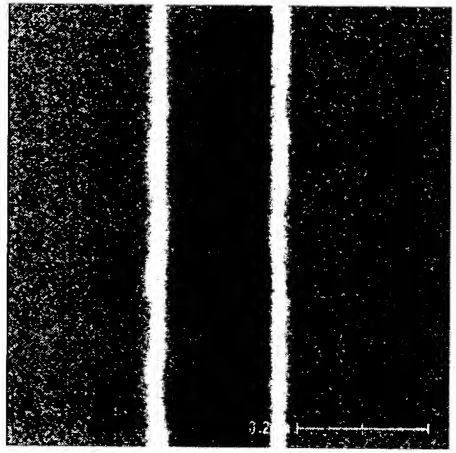


Strip 193nm
265nm IL K007547 - 550nm K007563T
TM99DF_TDF_V01
Trench 150nm
E=9 mj/cm2/0.1
F=0.1/0.1
NA 0.63 Sigma 0.5 **Na 2X rework**

193nm TIS Rework

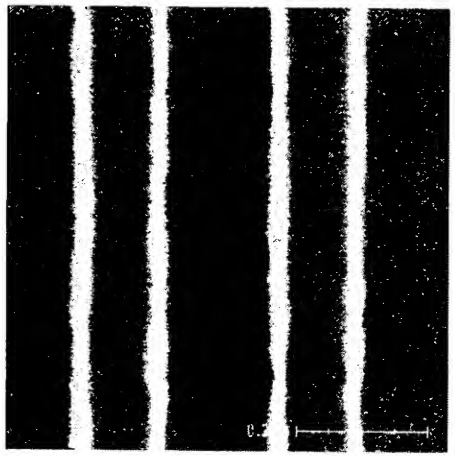
T010385 D22 RER600

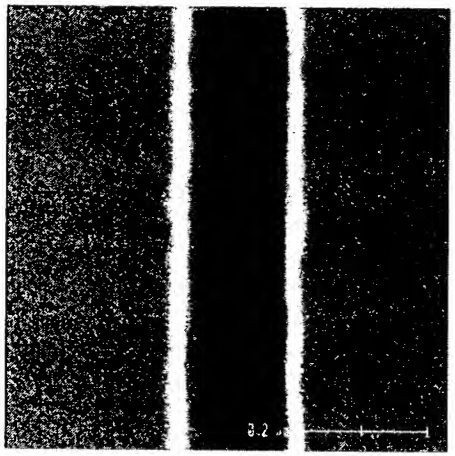




One bake steps before exposure after rework:
* 105°C/90"

T000058 D15 RER651

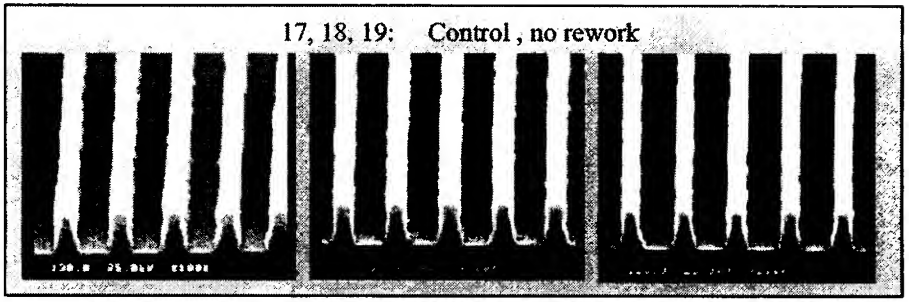




TIS2000IL-5 Rework (193nm)

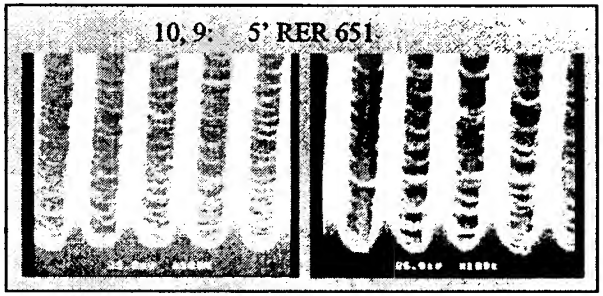
130 nm images after 1 x rework

Test Rework Chemistries



Chemical	Strip Time [minutes]	Dehydration Bake Temperature [°C]	Results
PGMEA	5	105	lifting
PGMEA	5	205	lifting
PGMEA	0.5*	None*	scumming
PGMEA/MPK 99/1	5	105	lifting
PGMEA/EL 90/10	5	105	scumming
RER 651	5	105	scumming
RER 651	10	105	scumming
RER 651	20	105	scumming

* Track strip process



WR12123290

TIS2000IL-5 Rework (193nm)

130 nm images after 1 x rework

Effect of Processing Steps on UL

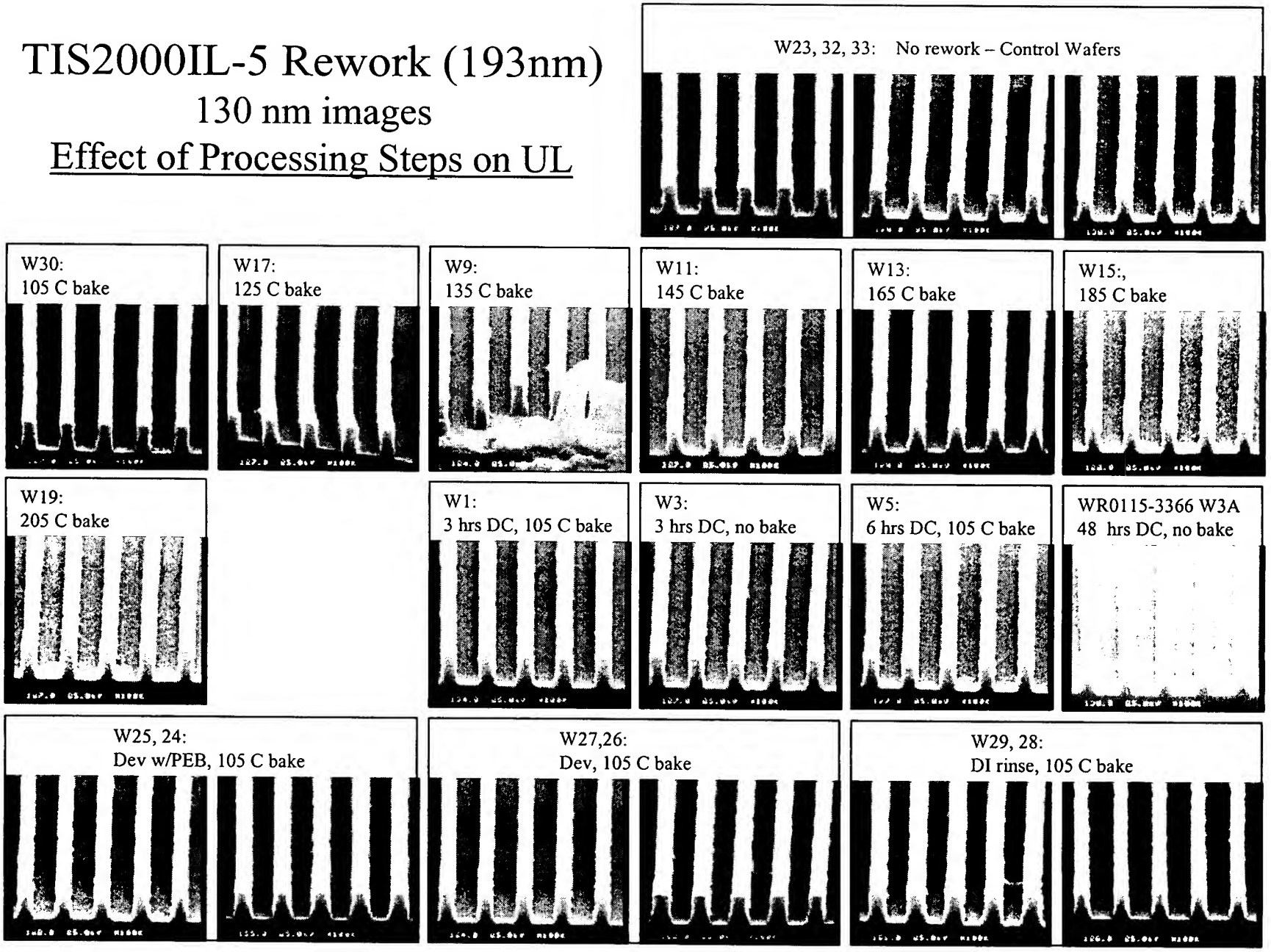
UL left in 'Dirty Chase' (DC) [hours]	Dehydration Bake Temperature [°C]	Develop/rinse	Results
3	105	none	good
3	none	none	good
6	105	none	good
48	none	none	good
0	105	none	good
0	125	none	good
0	135	none	good
0	145	none	good
0	165	none	good
0	185	none	good
0	205	none	good
0	105	Develop w/PEB	good
0	105	Develop w/oPEB	good

In this experiment the 1st imaging step was skipped.

TIS2000IL-5 Rework (193nm)

130 nm images

Effect of Processing Steps on UL



WR01143363

TIS2000IL-5 Rework (193nm)

130 nm images

PGMEA and Processing Revisited

UL cure time [seconds] @ (205 C temp)	Strip Time [minutes]	Dehydration Bake Temp. [C]	Other Treatment	Results
60	5	105		good
90	5	105		good
120	5	105		good
70	1	105		good
70	3	105		good
70	5	105		good
70	5	150		good
70	5	180		good
70	5	150	30" HF dip after strip	scum
70	5	150	1st IL coat skipped	good

In this experiment we attempted to make PGMEA as stripping solution work by modifying base processes.

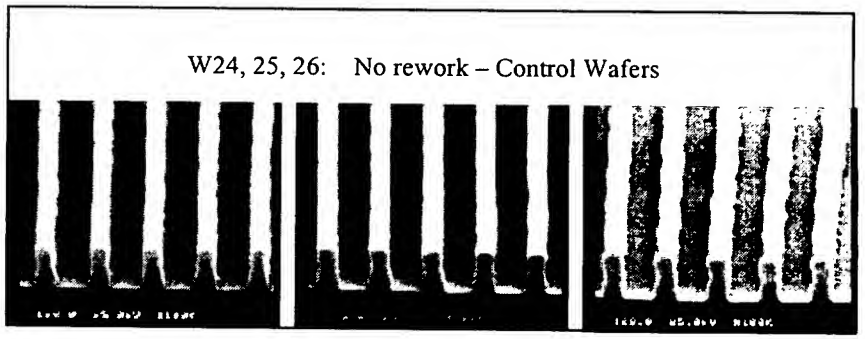
Unless otherwise noted, the 1st IL was coated only. To save time exposure and development were skipped.

TIS2000IL-5 Rework (193nm)

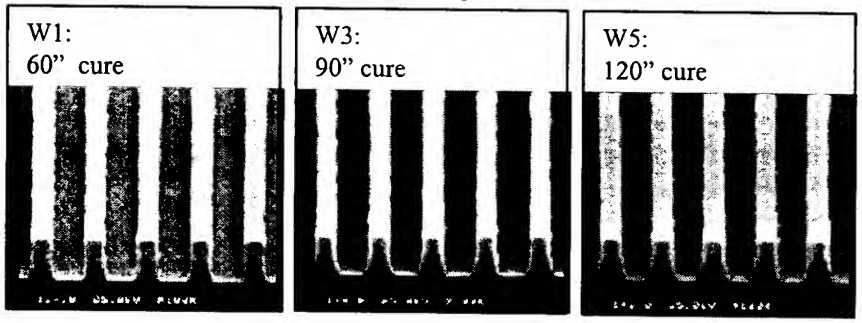
130 nm images

PGMEA and Processing Revisited

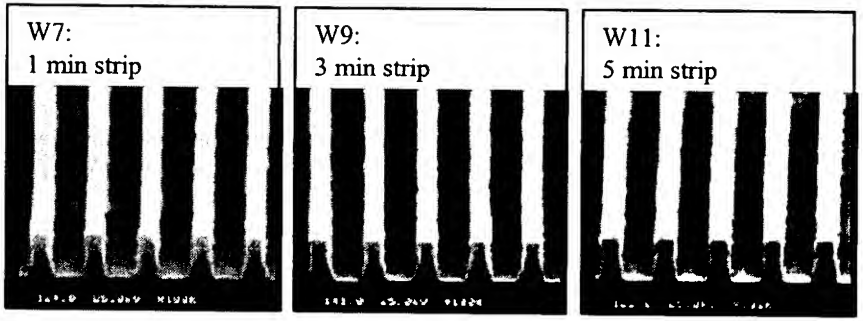
Control



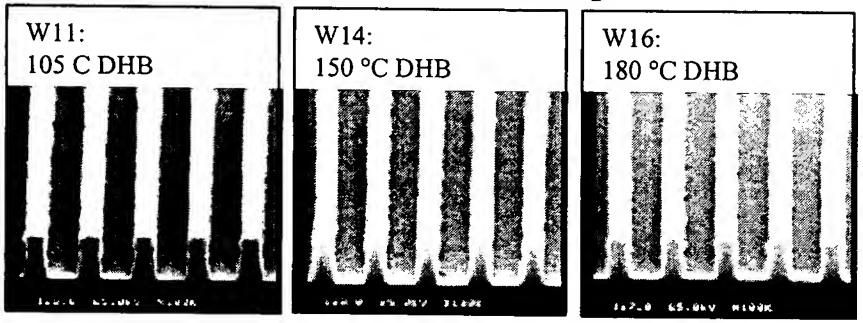
UL Curing Time



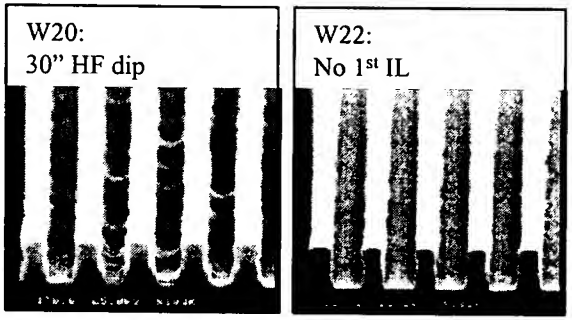
Strip Time



Dehydration bake temp



Other



WR 01253416

TIS2000IL-5 Rework (193nm)

130 nm images

Rework Chemistries Revisited

Chemical	Other Treatment	Results
PGMEA	1st IL exp/dev	scum
PGMEA	1st IL PEB	good
PGMEA		good
PGMEA/MPK 99/1		good
PGMEA/EL 90/10		good
RER 651		good

Unless otherwise noted, the 1st IL was coated only. Based on earlier experiments the DHB temperature was changed to 150 C, and strip time was 2 minutes.

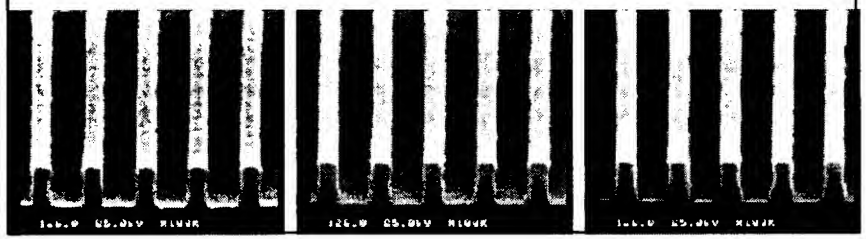
TIS2000IL-5 Rework (193nm)

130 nm images

Rework Chemistries Revisited

Control

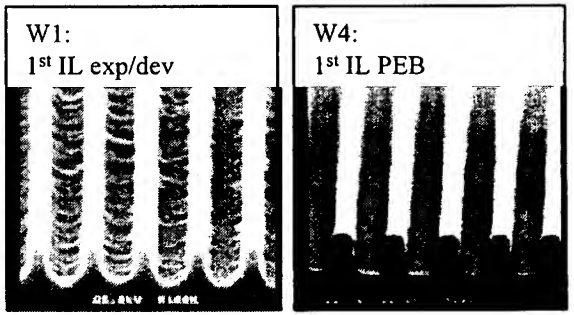
W21, 22, 23: No rework – Control Wafers



PGMEA and Image Step

W1:
1st IL exp/dev

W4:
1st IL PEB



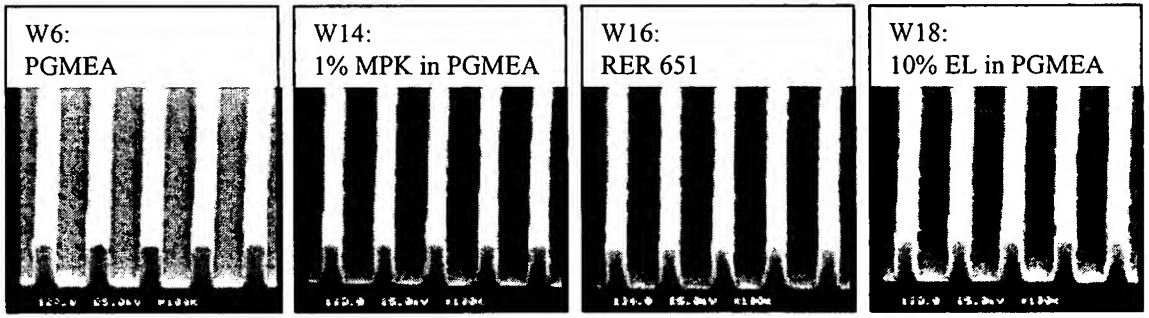
Stripping Chemistry

W6:
PGMEA

W14:
1% MPK in PGMEA

W16:
RER 651

W18:
10% EL in PGMEA



WR 0207-3489

TIS2000IL-5 Rework (193nm)

130 nm images

Imaging Process and HF Dipping

1st IL coat?	Imaging Process Steps	HF dip [minutes]	Results
N	expose	none	good
Y	expose	none	good
Y	exp/PEB	none	good
Y	exp/PEB/dev	none	footing
N	none	1	good
N	none	2	good
N	none	3	good

What in the imaging process caused the failure after rework?

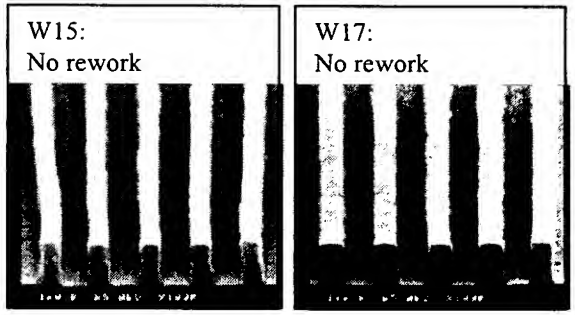
HF dip was done to see if acid formation during imaging has a negative impact on IL rework. If 1st IL was applied a 5' PGMEA strip, followed by a 150 C DHB was done.

TIS2000IL-5 Rework (193nm)

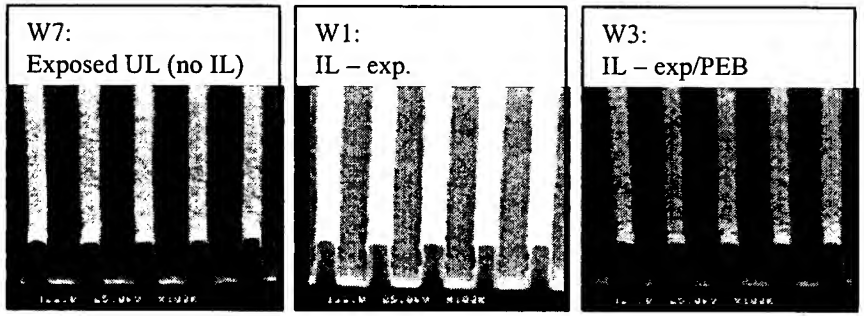
130 nm images

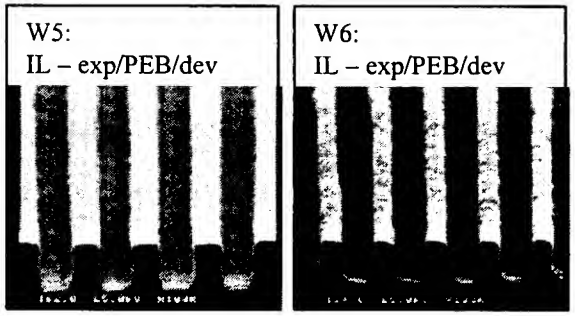
Imaging Process and HF Dipping

Control

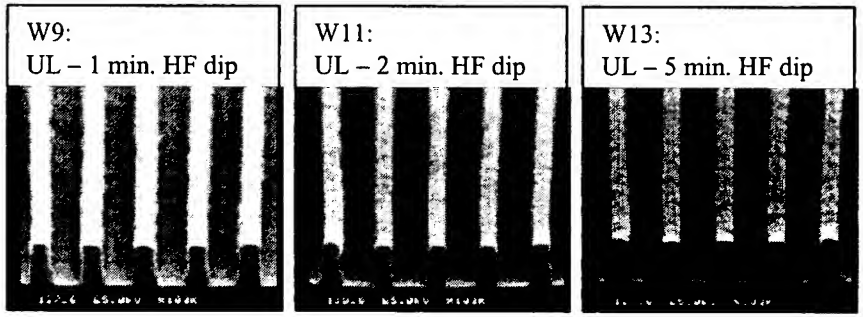


Imaging Process





HF dipping



WR 0218-3525